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Structural and Optical Properties of Wurtzite InP/AlInP Core-Multishell Nanowires

Fumiya Ishizaka[1], Yoshihiro Hiraya[1], Katsuhiro Tomioka[1,2], Junichi Motohisa[1] and Takashi Fukui[1]

[1] Graduate school of Information Science and Technology and Research Center for Integrated Quantum Electronics (RCIQE), Hokkaido University, North 13 West 8, Sapporo, Hokkaido 060-8628, Japan
[2] Japan Science and Technology Agency (JST) – PRESTO, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan
Phone: +81-11-706-7173 E-mail: ishizaka@rciqe.hokudai.ac.jp

Abstract

We investigated the structural and optical properties of InP/AlInP core-multishell nanowires. Double heterostructures were fabricated in the AlInP shells by changing alloy compositions. Transmission electron microscopy revealed that the AlInP shell was grown with a wurtzite (WZ) structure on the side of the WZ InP core while it was grown with a zinc blende (ZB) structure on the top. The lattice constants of WZ InP core and WZ AlInP shell were also investigated by X-ray diffraction measurements. Position-dependent cathode luminescence studies showed that the WZ $Al_{0.4}In_{0.6}P$ shell had an emission energy of 1.7–1.9 eV, which is in the visible red region.

1. Introduction

Semiconductor nanowires (NWs) have been attracting much attention in recent years because of their potential applications in electronic and photonic devices. The unique feature of nanowires is that they can be grown with a wurtzite (WZ) crystal structure by properly adjusting the growth conditions [1], even though they are stable in the zinc blende (ZB) phase of the bulk crystal. This crystal structure engineering paves the way for novel device applications of nanowires because the crystal structure has a significant effect on the physical properties of semiconductor materials. It has been theoretically suggested for indirect band gap materials such as GaP and AlP that when their crystal phases are changed from ZB to WZ, their band gaps also change from indirect to direct, due to the zone folding effects [2]. This suggestion has been experimentally shown using WZ $Al_xGa_{1-x}P$ nanowires with $0 \leq x \leq 0.46$, indicating that the efficiency of light-emitting diodes (LEDs) can be increased [3]. However, there have been few experimental studies on other materials. According to the band structure calculations [2], WZ AlInP ternary alloys are expected to have direct band gaps in the entire compositional range, and are therefore promising for the red, amber, and yellow LEDs. However, structural and optical properties of WZ AlInP still have not been well investigated until now. Here, we report on the structural and optical properties of WZ InP/AlInP core-multishell nanowires grown by selective-area metal organic vapor phase epitaxy (SA-MOVPE).

2. Experimetal

An SiO_2 layer with a thickness of 20 nm was deposited on an InP (111)A substrate by plasma sputtering, and hexagonal-opening patterns were then defined by electron-beam (EB) lithography and wet chemical etching with buffered hydrofluoric acid (BHF). The SiO_2 patterns were designed to be a periodic array of openings with a diameter of about 150 nm and a pitch of 1.0 μm. The SA-MOVPE of nanowires was carried out in a horizontal low-pressure MOVPE system using trimethylaluminum (TMAl), trimethylindium (TMIn), and tertiarybutylphosphine (TBP) as source materials. Grown layers of the core-multishell nanowires are summarized in Fig. 1(a). For InP core growth, the growth temperature and growth time were 660°C and 15 min with a V/III ratio of 18. For AlInP shell growth, the barrier layers were grown 600°C and 5 min for each layer and the active layer was grown 600°C and 30 min. The partial pressure ratio of TMAl for the active layers, X_{TMAl} = [TMAl]/([TMAl]+[TMIn]), was changed to 0.05, 0.11, 0.18, 0.25 or 0.40. Those for the barrier layers were approximately 0.20 higher than X_{TMAl}. The grown structures were characterized using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). X-ray diffraction (XRD) measurements were performed on about 4 mm^2 area, where more than one million nanowires are included. Cathode luminescence (CL) measurements were carried out at 36K on a single nanowire.

3. Results and discussion

A schematic view and an SEM image of the grown InP/AlInP core-multishell nanowire for X_{TMAl} = 0.18 are shown in Figs. 1(a) and 1(b). The InP core was used as a template for transferring WZ structures to the AlInP shell. The AlInP barrier layers were fabricated to prevent electron-hole pairs from moving to the lower-bandgap InP core. The InP cap layer was grown in order to avoid oxidation of the AlInP shell. From Fig. 1(b), the average height and total diameter of the core-multishell nanowires were approximately 2.6 μm and 425 nm, respectively. For the other four samples, they were in ranges of 2.5–2.8 μm and 385–440 nm.

Figures 2(a)–2(c) show cross-sectional TEM images of an InP/AlInP core-multishell nanowire and locally magnified high resolution TEM images at the top and middle of the nanowire, respectively. The corresponding selective area electron diffraction (SAED) patterns are shown in Figs. 2(d) and 2(e). From these images, the crystal structures of three parts of the nanowire can be investigated. The AlInP shell on the top of the InP core had a ZB structure with rotational twins around the <111> axis. Both the template InP core and the AlGaP shell on the side of the InP core had WZ structures. These results indicate that the

WZ structure can be transferred in the radial <-211> direction while it was changed to a more stable ZB structure in the axial <111>A direction, as in the case of InP/GaP core-shell nanowires [4].

To investigate the crystal structures of the nanowire assembly, we recorded reciprocal space mappings (RSMs) of the nanowires using XRD measurements. An RSM of InP/AlInP core-multishell nanowires for X_{TMAl} = 0.18 is shown in Fig. 3(a). The WZ (10-15) and ZB (331) peaks were observed for the InP core and substrate, and the WZ (10-15) and ZB (224) twin peaks were observed for the AlInP shell. The strong intensity of the WZ InP (10-15) peak indicates that the InP core has a high crystal quality in the WZ structure. The WZ AlInP (10-15) peak was relatively broad along the Q_z axis, which implies that WZ AlInP shell had several stacking faults resulting from the lattice mismatch between InP and AlInP. The ZB (224) twin peak for AlInP was attributed to the ZB AlInP shell with rotational twins grown on the top of the InP core. Figures 3(b) and 3(c) show axial and radial lattice constants of the WZ InP core and AlInP shell plotted with respect to the Al composition, which were calculated from the maximum peak positions of (10-15) reflections. The calculated Al compositions had compositional variations of 0.01–0.04 from the corresponding X_{TMAl}. The calculated lattice constants of both InP core and AlInP shell tend to have a larger difference from the relaxed lattice constants at lower X_{TMAl}. This result shows the presence of strain between the core and shell at low X_{TMAl}.

To investigate the optical properties of WZ AlInP, we carried out position-dependent CL measurements on a single nanowire at 36K. Figure 4 shows averaged CL spectrum obtained from WZ InP/AlInP for X_{TMAl} = 0.40. The emission peaks for the WZ InP core were 1.53 and 1.49 eV, which correspond to the WZ InP bandgap and type II ZB/WZ junctions, respectively [5]. The multiple emission peaks for the WZ AlInP shell appeared around 1.7–1.9 eV, which may originate from local composition variations in the nanowire. This result is a first step toward visible red-amber emissions using WZ AlInP materials.

4. Conclusions

We fabricated WZ InP/AlInP core-multishell nanowires with double heterostructures by changing alloy compositions. TEM analysis revealed that the AlInP shell was grown with a WZ structure at the side, while a ZB structure at the top. XRD measurements showed that the WZ AlInP shell had several stacking faults, and that the strain between the core and shell were observed at low X_{TMAl}. The WZ AlInP shell for X_{TMAl} = 0.40 had CL emissions in the visible red region.

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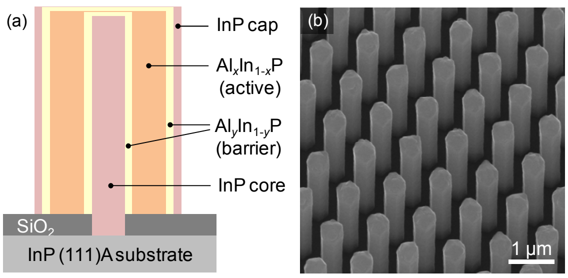

Fig. 1 (a) Schematic view of grown layers of the core-multi shell nanowire. (b) 30°-tilted SEM image of the nanowires for X_{TMAl} = 0.18.

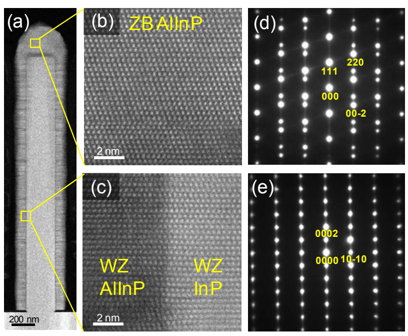

Fig. 2 (a) Overall TEM image of the nanowire for X_{TMAl} = 0.18. High resolution TEM images (b) at the top of the nanowire and (c) at the interface of InP core and AlInP shell. The corresponding SAED patterns at the (d) top and (e) middle of the nanowire, showing a ZB structure and a WZ structure, respectively.

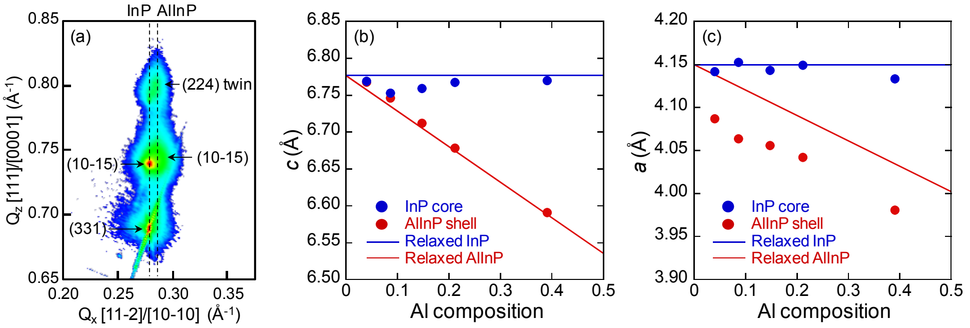

Fig. 3 (a) XRD RSM of InP/AlInP core-multishell nanowires for X_{TMAl} = 0.18. (b) Axial and (c) radial lattice constants of the WZ InP core and AlInP shell calculated from the maximum peak position of (10-15) reflections. Blue and red solid lines represent the WZ lattice constants of relaxed InP and AlInP calculated from their ZB lattice constants when they are converted from ZB to ideal WZ.

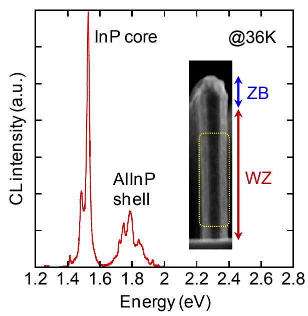

Fig. 4 Averaged CL spectrum obtained by yellow dotted circle of a single InP/AlInP core-multi shell nanowire for X_{TMAl} = 0.40.